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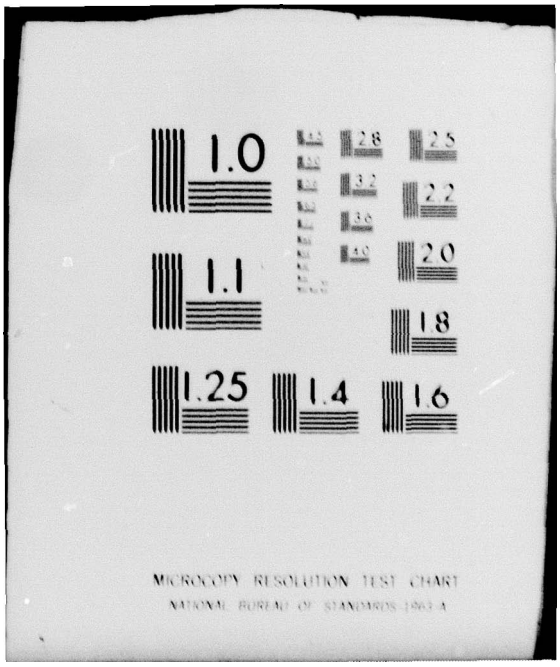
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Volatile Metal Chelates, Metal Chelate Sorbents, Molybdenum, Aluminum, NMR Shift Reagents, Selective Electron Capture Sensitization, SECS, Open-Pore Polyurethane, Environmental Analyses, PAH, Pyrene, Nitrates, NO_x, Jet Engine Exhaust.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Results are reported from a trace level analysis research program enveloping volatile metal chelate chemistry, gas chromatography, and environmental analysis. The overall thrust of the program was to develop sensitive and selective analytical techniques for a variety of samples. The methods employed involved various combinations of sample collection and concentration, derivatization and separation, and, finally, detection. Examples of the measurements considered include molybdenum and aluminum by a

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metal chelate derivatization/atomic absorbtion spectrophotometric technique, polynuclear aromatic hydrocarbon concentration on open-pore polyurethane (OPP) followed by liquid chromatographic analysis, herbicide separation on OPP columns, and nitrate ion and nitrogen oxide analysis by a derivatization/electron capture technique.

A metal chelate containing material has been synthesized for use as a selective sorbent. The usefulness of the electron capture detector has been advanced by the addition of nitrous oxide to the carrier gas. With this technique, Selective Electron Capture Sensitization (SECS), additional sensitivity has been found for many compounds which normally are not detected by the electron capture detector.

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New chemical analysis techniques have been studied in three separate, but often interrelated areas. Volatile metal chelates have been synthesized and studied with a view towards improving the sensitivity of quantitative analysis for molybdenum, chromium and aluminum, separating enatiomeric isomers, and developing selective sorbent materials. Chromatographic systems have been fabricated and studied in order to evaluate the performance of innovative separation and detector schemes. Various environmental studies have been made to develop analyses for several species, including polynuclear aromatic hydrocarbons (PAH), nitrogen oxides, and several anionic species.

Volatile Metal Chelates

A comprehensive overview of volatile metal chelates has been published (9) and a more specific treatment of such complexes as fuel antiknock additives has been given (13). Various structural and bonding parameters have been related to the NMR shift reagent properties of europium complexes (11).

Several monomeric, Mo (VI) β-diketonates have been synthesized and studied to assess their potential in making more sensitive atomic absorption measurements of Mo in an N_2O-C_2H_2 flame (15). Molybdemum complexes of 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), 3-(trifluoromethylene)-d-camphor (Hfacam), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod), for example, show enhanced sensitivity in a N_2O-C_2H_2 flame over ammonium phosphomolybdate. When n-butylacetate is the solvent a 2-fold enhancement is found and the detection limit (1% absorption) is 0.065 μg/mL. This enhancement is in addition to the enhancement observed when

changing to an organic solvent from water. Similar, but smaller enhancements are observed in analogous experiments with Al and Cr chelates (15,16).

A lanthanide metal chelate, tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium(III), $Eu(fod)_3$, was used as a pre-chromatographic column which is specific for oxygenated compounds (17). The metal chelate was sorbed onto porous silica and used in a subtractive technique to remove oxygen containing interferences in a gas chromatographic separation. The technique also has been used to remove solvent methanol from a sample, yielding a chromatogram free of a solvent peak. This work also demonstrates the possibility of thermally desorbing compounds from this metal chelate sorbent, resulting in highly class-specific analyses.

Separation of optically active isomers have been attempted using chiral lanthanide chelates. Glass capillary columns were deactivated with 3-aminopropyltriethoxysilane followed by diketene. This procedure is intended to cover the glass surface with β-ketoamide functional groups. A chiral complex, such as $Eu(facam)_3$ could then become bonded to the glass surface via a ligand exchange reaction with the modified glass surface. To date, however, no successful separations of optical isomers have been attained with columns prepared in this way.

Chromatographic Systems

Enhanced electron capture detector sensitivity for certain compounds is possible when N_2O is added to N_2 carrier gas (14). This sensitization is selective for compounds which can undergo

ion-molecule reactions with O^- and NO^- that are generated *in situ* in the detector when N_2O is present. Enhanced response by Selective Electron Capture Sensitization (SECS) has been observed for methane, ethane, n-propane, n-butane, n-pentane, n-hexane, benzene, ethanol, methylisobutylketane, hydrogen, and carbon dioxide. Several hydrocarbons are detectable at the picogram level. With the SECS detector, a 5000-fold increase in response is found for CO_2, a 10-fold increase for methane, and a 40-fold increase for hydrogen.

Open pore polyurethane (OPP) chromatographic media have been developed in two ways. Improved gas chromatographic column behavior has been observed with respect to peak shape and temperature stability (4). A column prepared using a hydroxyl to isocyanate functional group ratio of approximately 2:1 yields good separation and symmetrical peaks for polar compounds, including alcohols. OPP columns coated with Carbowax 20M show improved temperature stability in the 150°C to 225°C range and have been used for separation of the herbicides methyl-2,4-D (methyl 2,4-dichlorophenoxyacetate) and methyl Fenac (methyl 2,3,6-trichlorophenylacetate).

Pre-concentration columns of OPP have been tested for ion-exchange properties, solvent compatabilities, and ability to preconcentrate polynuclear aromatic hydrocarbons from water (5,7). Pyrene recovery is nearly 100% when 1 L of solution containing 1 µg of pyrene is passed through a 0.3 x 5 cm column and eluted with 5 mL of methanol.

A gas chromatographic injector attachment has been developed and fabricated for use with samples that are concentrated on porous polymer sorbents (10). The device allows insertion, heating, and removal of a polymer sorbent trap from a chromatograph injection port in a convenient manner.

Preliminary studies have been made to determine the feasibility of using microwave energy as a selective thermal heater for various stationary phases that could be used in gas chromatographic separations. A series of selected chromatographic liguid phases was subjected to microwave excitation; the results of these experiments indicate that the various phases are heated roughly in proportion to their polarity.

Environmental Studies

A method for the analysis of nitrates and nitrites has been developed for use with a wide variety of samples, including human saliva, blood, drinking water and airborne particulates (3,8). Aqueous nitrate ion is first converted to nitrobenzene in the presence of a catalyst. Nitrobenzene is then quantified by electron capture gas chromatography. Appropriate sample pretreatment allows a similar determination to be made for nitrite ion and other oxides of nitrogen. Nitrite ion in blood or saliva can be quantified at the 0.1 ppm (w/w) level using approximately a 0.05 mL (one drop) sample. Sample collection parameters and appropriate modifications of this technique have been determined to allow collection and measurement of particulate nitrate, gaseous nitric acid, and nitrogen dioxide in ambient air (8,12). An appropriate series of filter media affords a pre-separation of these species. More recent work has shown that a Teflon particulate filter is an important improvement over a glass fiber filter because Teflon does not collect nitric acid.

Jet engine exhaust analyses have been performed which allow determination of compound classes (6). A simple gas chromatographic technique utilizing two analytical columns has been developed for the determination of saturated, olefinic, and combined oxygenated-aromatic

fractions of jet engine exhaust which is collected on a dual sorbent trap containing Tenax GC and Carbosieve B. Experimental results have been obtained with synthetic exhaust hydrocarbon mixtures and jet combustor exhaust samples.

A study of beryllium concentrations in ambient air particulate matter has been concluded (1).

Chromium levels in blood serum have been determined using a coupled gas chromatograph - microwave emission detector (2). Samples are prepared by low temperature ashing of serum followed by chelation of chromium with 1,1,1-trifluoro-2,4-pentanedione [H(tfa)] to form the volatile complex $Cr(tfa)_3$. A benzene extract of the complex is chromatographed and detected by a microwave emission detector. The detection limit is 9×10^{-13} g of chromium per μL of benzene.

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